Experimental

Data collection and refinements

A single crystal of **1**, 0.20 × 0.15 × 0.11 mm, was selected for measurement. Diffraction data were collected on an automated CCD diffractometer, Rigaku AFC-8 Mercury, on PF-AR NW2 beam line at KEK using 0.7000 Å radiation with an oscillation method at 106K. Bragg spots on the imaging plates were integrated up to $\sin\theta / \lambda = 0.97$ Å^{-1}, and scaled with the program HKL2000.[1] Measured and independent reflections, R_{int} and completeness were 124265, 22754, 0.0401 and 0.915, respectively.

The reported structure[2] was used as an initial model. Anomalous scattering factors and X-ray absorption coefficients were taken from references 3 and 4, respectively. Following the refinements, high order refinements were carried out using all 9818 independent reflections with $\sin\theta/\lambda \geq 0.60$ Å^{-1} with the program SHELXL97.[5] Positions of hydrogen atoms were constrained to have C–H distances of 1.092, 1.083 and 1.059 Å for methylene, aromatic and methyl groups, respectively.[6] Refinements of multipole expansion method using the Hansen-Coppens multipole formalism[7] and topologaical analyses based on resulted parameters were performed with the XD package.[8] Refinement was carried out against 6915 independent reflections of $\sin\theta/\lambda \leq 0.8$Å^{-1} with $I > 3\sigma(I)$ based on F^2. At the first stage of the refinements, atomic coordinates and U_{ij} of non-hydrogen atoms were fixed on those of the high order refinement, and U_{iso} of hydrogen atoms were fixed on $1.2U_{eq}$ and $1.5U_{eq}$ of each parent C atom for methylene and aromatic, and methyl groups, respectively. At the first stage of the refinements, the population parameters, P_v, $P_{lm\pm}$ of non-hydrogen atoms and scale were refined. Levels of multipoles were raised stepwise up to hexadexapole and octupole for Zr and C atoms, respectively. On the refinements of the population parameters were constrained by assuming the molecular C_2 symmetry. At the second stage, radial screening parameters, κ and κ' for non-hydrogen and hydrogen atoms were refined. At the third stage, the levels of multipoles were raised stepwise up to hexadecapole, octupole and dipole along the bond for Zr, C and H atoms, respectively. After those refinements, the second and third strategies were repeated twice and finally the P_v, $P_{lm\pm}$, κ, κ', coordinates of the non-hydrogen atoms and temperature factors and scale were refined. The positions of the H atoms were constrained to have C–H distances of 1.092, 1.083 and 1.059 Å for methylene, aromatic and methyl groups, respectively. The number of parameters in the final cycle of the refinements was 425. A molecule electro-neutrality constraint was applied all through the refinements.

References

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